Synthesis of *N*-(2-Pyranyl)- and *N*-Cyclohexylindole Derivatives via Stereoselective Addition of Indole Nucleophiles to Organomolybdenum Complexes

Emelie Bjurling,[†] Maria H. Johansson,[‡] and Carl-Magnus Andersson*[,§]

Departments of Organic Chemistry 1 and Inorganic Chemistry 1, Chemical Center, Lund University, P.O. Box 124, S-221 00 Lund, Sweden, and Synthetic Chemistry, ACADIA Pharmaceuticals A/S, Fabriksparken 58, DK-2600 Glostrup, Denmark

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Indol-1-yl-substituted dihydropyranyl- and cyclohexenylmolybdenum complexes were obtained via nucleophilic addition of a variety of substituted indoles to cationic (pyran)- and (cyclohexadiene)molybdenum complexes. The efficiency of these addition reactions was found to be highly dependent upon the substitution pattern in the nucleophile. Oxidative decomplexation with iodine smoothly delivered the corresponding allylic iodide in good yield. Complex **6b** was characterized by X-ray crystallography.

Introduction

The glycosyl- or pyranylindole structural motif is common to a variety of pharmacologically interesting natural products. The best known examples, staurosporine and rebeccamycin (Figure 1), are both protein kinase C inhibitors, and especially the exceptional potency of the former has recently spurred intense synthetic efforts toward clinically useful analogues.[1] Staurosporine has an indolocarbazole moiety attached to a highly functionalized pyran ring through both nitrogens, one of which connects to a quaternary carbon. The total synthesis of this challenging target was recently accomplished by Danishefsky et al.[2] and Wood et al.,[3] who both employed strategies involving alkylation of advanced indolocarbazole precursors. As part of a program addressing the application of organometallic templates within medicinal chemistry, we contemplated a route to staurosporine derivatives based on stereoselective, stepwise introduction of indole building blocks into a pyranylmolybdenum complex followed by oxidative coupling of the indole fragments.

The utilization of stoichiometric transition-metal π-complexes for the stereocontrolled construction of fairly complex organic molecules[4,5] has been demonstrated primarily by Pearson[4] and Liebeskind.[6,7] The coordination of a substrate to a metal moiety generally directs all incoming nucleophiles to the face of the π-ligand opposite the metal, an *anti*-directing effect.[8] With cyclic π-ligand substrates attached to iron or molybdenum centers, this mode of reaction facilitates the introduction of multiple substituents in a *cis* fashion.[8] Importantly, these metal-assisted additions have proven particularly valuable for the construction of quaternary centers.[9] However, the opportunity to apply heteroatom nucleophiles in such reactions has remained essentially unexplored. Herein, we describe the successful addition of indole derivatives to cationic (pyran)- and (cyclohexadiene)molybdenum complexes and also dem-

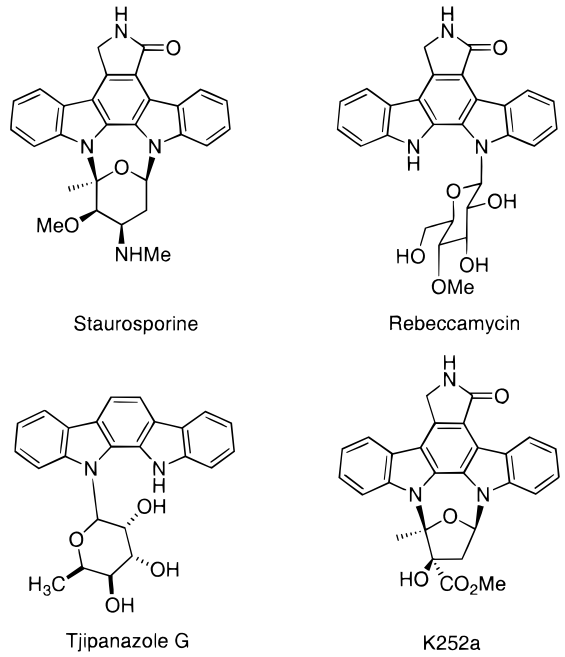

Figure 1.

* To whom correspondence should be addressed. E-mail: cma@acadia-pharm.com.
[†] Organic Chemistry 1, Lund University.
[‡] Inorganic Chemistry 1, Lund University.
[§] ACADIA Pharmaceuticals.

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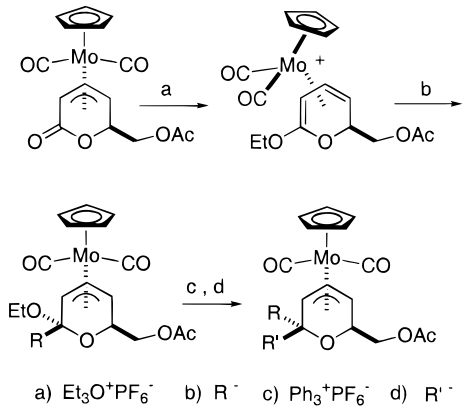

Figure 2.

onstrate successful release of the organic product via oxidative demetalation.

Results and Discussion

(2,2-Dialkylpyranyl)- and (2,2,6-Trialkylpyranyl)-molybdenum Complexes. Nucleophilic addition to cationic diene molybdenum complexes has been performed with a variety of organometallic carbon nucleophiles,[6−9,10−12] including Grignard reagents, as well as lithium− or zinc−copper reagents. An elegant route to disubstituted cyclic allylic ligands has been developed by Faller[11] and Pearson.[13,14] In this procedure, sequential hydride abstractions using trityl salts and nucleophilic addition reactions were shown to deliver carbanions *anti* to molybdenum in a highly regio- and stereocontrolled fashion. When cyclohexenyl complexes were used as substrates in these reactions, the products formed were *cis*-1,5-disubstituted complexes.[11,13]

Liebeskind has shown that nucleophilic addition of organolithium or -magnesium reagents to (η^5-cyclopentadienyl)dicarbonyl(η^4-2*H*-pyran)molybdenum tetrafluoroborate proceeds with 60−90% yield of the allylic complex. Hydride abstraction followed by addition of an alkyl- or aryllithium reagent then gave a 2,6-*cis*-disubstituted complex in good yield.[7] Access to 2,2,6-trisubstituted pyranylmolybdenum complexes[6] by using in a similar sequence (η^5-cyclopentadienyl)dicarbonyl-[(3*S*,6*R*)-(3,4,5-η)-6-(acetoxymethyl)-2-oxo-5,6-dihydro-2*H*-pyran-5-yl]molybdenum as the starting material (Figure 2) has also been demonstrated. Alkylation of the carbonyl group using Meerwein's reagent gave a cationic diene complex, which underwent nucleophilic additions in 60−95% yields. Further abstraction of the ethoxy group with trityl hexafluorophosphate proceeded with nearly quantitative yield of the diene cation, which with excess Grignard reagents gave trisubstituted pyranyl complexes in 60−70% yield.

We initiated our experiments by addressing the previously unexplored sequential introduction of three

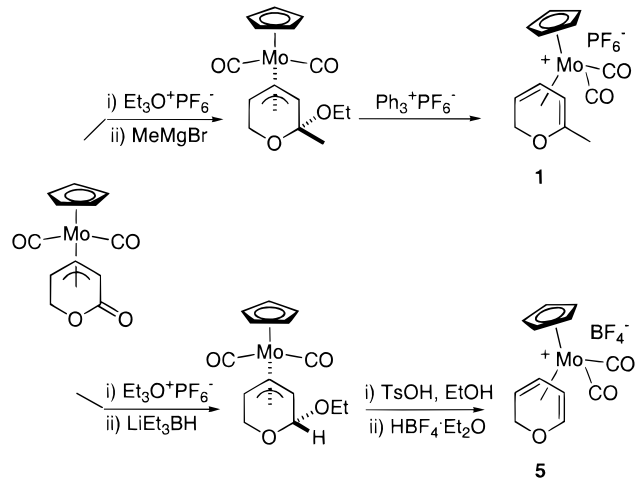

Figure 3.

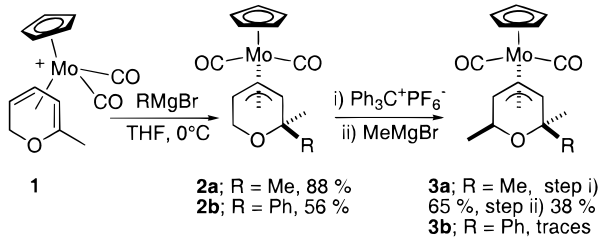

Figure 4.

substituents into the parent (dihydropyranyl)molybdenum framework. Preliminary experiments entailed the addition of carbon nucleophiles to racemic (η^5-cyclopentadienyl)dicarbonyl[6-methyl-(3,4,5,6-η)-2*H*-pyran]molybdenum hexafluorophosphate (**1**), which in turn was synthesized from the lactonylmolybdenum complex as shown in Figure 3.[6] The cationic complex was dissolved in THF, and MeMgBr (5 equiv) or PhMgBr (4 equiv) was added at 0 °C (Figure 4). The addition of MeMgBr to **1** gave the allylic complex **2a** in 88% yield and the addition of PhMgBr produced **2b** in 56% yield. The allylic substrate **2a** then underwent hydride abstraction with Ph_3CPF_6 in CH_2Cl_2 to form the cationic diene complex, which was isolated in 65% yield. Addition of the methyl Grignard reagent to **2a** gave the trisubstituted allylic complex **3a** in modest yield (Figure 4). The phenyl-substituted **2b**, on the other hand, failed to return any isolable diene cation, and a one-pot sequence yielded only trace amounts of the desired **3b** (vide infra).

Addition of Indole Nucleophiles to Cationic (2*H*-Pyran)- and (Cyclohexadiene)molybdenum Complexes. To our knowledge, only a few examples of the addition of nitrogen nucleophiles to (diene)molybdenum complexes have been reported. In the single intermolecular case,[15] several amines were shown to provide good yields of addition products with the highly electrophilic $Tp(CO)_2$(cyclopentadienone)molybdenum cation in the absence of additional base. Intramolecular addition[16] of a tosyl amide to a cationic allylic CpMo(CO)(NO)(cyclohexenyl) complex in the presence of triethylamine to form a heterobicyclic derivative has also been achieved. Indole has previously been shown

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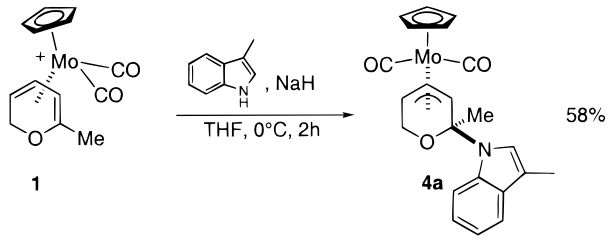


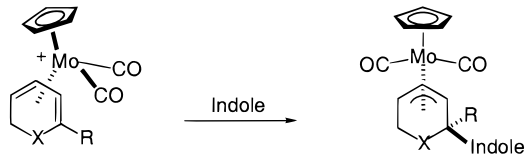
Figure 5.

to react with tricarbonyl(cyclohexadienyl)iron or -ruthenium,[17] via electrophilic attack of the dienyl cation at the C_3 position of indole.

Our initial attempts to synthesize a [2-(indol-1-yl)-pyranyl]molybdenum complex utilized 3-methylindole in order to avoid possible complications caused by an ambident nucleophile.[18] Deprotonation of the amine was best achieved with sodium hydride, since MeMgBr as base produced methylated complex in preliminary runs. A slight excess of NaH and 3-methylindole were stirred in THF at room temperature for 30 min before the reaction mixture was cooled to 0 °C and the cationic 2*H*-pyran complex **1** was added. By this procedure, the reaction returned adduct **4a** (Figure 5) in 58% yield, which compares favorably with yields reported for the addition of carbon nucleophiles to similar complexes.[6,7] Interestingly, the corresponding reaction employing unsubstituted indole anion returned exclusively the N-alkylated product **4b**, which could be isolated in 66% yield (Table 1). In contrast to (cyclohexadienyl)iron or -ruthenium complexes,[17] molybdenum complex **1** failed to alkylate indole in the absence of base. Although the allylic products **4a**,**b** were found to be fairly acid labile, isolation of analytically pure material was possible, provided that triethylamine was present during extractive workup and column chromatography. The propensity for protolytic degradation, back to free indole and **1**, observed with **4a**,**b** prompted us to explore the use of less electron-rich indoles, such as those in entries 3−5 of Table 1. However, the cyano-, formyl-, and nitro-substituted indoles failed to react with cation **1** under the present conditions, presumably as a result of the much weaker nucleophilicity of these indole anions. Several modifications were explored using 3-formylindole as the nucleophile, but a variety of solvents, elevated temperatures or the use of crown ethers all failed to promote the addition reaction. Interestingly, 2-indolinone turned out to add to cation **1** to provide exclusively the C_3-alkylated[19] product **4f** in 40% yield. On the other hand, 2,3-indolinedione (entry 7) failed to react with **1**.

Recognizing the potentially problematic lability of the products derived from **1** in subsequent steps, we turned to the substrates (η^5-cyclopentadienyl)dicarbonyl[(3,4,5,6-η)-2*H*-pyran]molybdenum tetrafluorophosphate (**5**) and (η^5-cyclopentadienyl)dicarbonyl[(1,2,3,4-η)-cyclohexadiene]molybdenum hexafluorophosphate (**7**). We reasoned

Table 1. Addition of Substituted Indoles and Related Compounds to Cationic Molybdenum Complexes[a]



1 X = O, R = Me
5 X = O, R = H
7 X = CH_2, R = H

4 X = O, R = Me
6 X = O, R = H
8 X = CH_2, R = H

entry	complex	indole	product	yield[c] (%)
1	**1**	3-methylindole	**4a**	58
2	**1**	indole	**4b**	66
3	**1**	3-formylindole	**4c**	0
4	**1**	5-nitroindole	**4d**	0
5	**1**	3-cyanoindole	**4e**	0
6	**1**	2-indolinone[b]	**4f**	40
7	**1**	2,3-indolinedione	**4g**	0
8	**1**	3-(hydroxymethyl)indole	**4h**	41
9	**5**	3-methylindole	**6a**	54
10	**5**	3-cyanoindole	**6b**	70
11	**5**	3-formylindole	**6c**	47
12	**7**	3-methylindole	**8a**	42
13	**7**	3-cyanoindole	**8b**	61

[a] The indole derivative was stirred with NaH in THF for 30 min to 1 h. The solution was cooled to 0 °C, whereupon the cationic diene complex was added. Stirring was continued at 0 °C for 2−3 h. [b] DMF was used as solvent. [c] Isolated yields after silica gel chromatography or recrystallization.

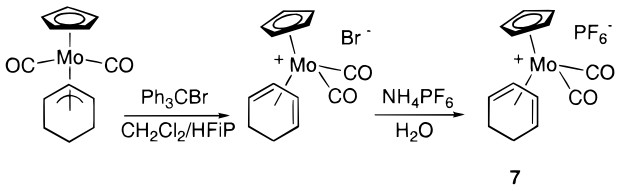


Figure 6.

that either removing the methyl group or substituting methylene for oxygen in **1** would enhance the reactivity toward nucleophiles and possibly concurrently decrease the lability of the product allylic complexes. While the single-step procedure[7] leading to cation **1** unexpectedly proved unreliable for the analogous preparation of **5**, the alternative two-step procedure,[6] involving epimerization and treatment with $HBF_4 \cdot Et_2O$, returned good yields of the latter (Figure 3). The cyclohexadiene complex **7** was synthesized from the corresponding cyclohexenyl complex through hydride abstraction with Ph_3CBr in dichloromethane in the presence of hexafluoro-2-propanol,[20] as shown in Figure 6. The comparatively low solubility of the bromide in THF necessitated exchange of the counterion for hexafluorophosphate, which occurred conveniently and quantitatively in water. The cations **5** and **7** indeed afforded the desired addition products also with less nucleophilic indole anions, such as those derived from 3-formyl- and 3-cyanoindole. Yields were, in fact, higher from reactions employing electron-poor nucleophiles (compare, for example, entries 9, 10 or 12, 13), possibly as a consequence of more facile isolation and purification. The products **6** and **8** were generally found to be more stable than

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(19) Alkylation of 2-indolinone usually returns mixtures of C3- and N1-alkylation products. Selective C3-alkylation has been achieved with 2-indolinone dianion; see: Kende, A. S.; Hodges, J. C. *Synth. Commun.* **1982**, *12*, 1.
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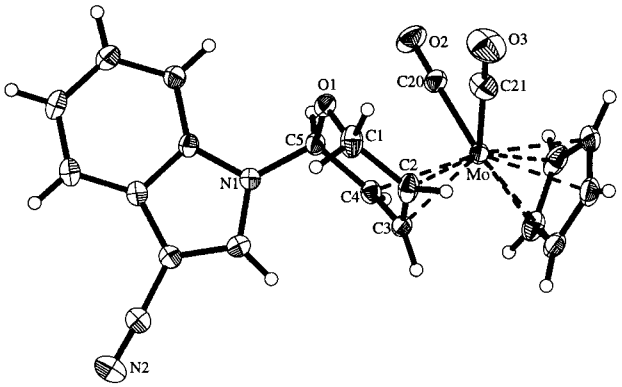

Figure 7. Structural view of complex **6b** showing the thermal ellipsoids at 30% probability (DIAMOND version 2.1). Selected bond distances (Å): C5−N1 = 1.484(2), Mo−C4 = 2.334(2), Mo−C3 = 2.202(2), Mo−C2 = 2.370(2), Mo−Cp = 2.315(2)−2.382(2), Mo−C20 = 1.940(2), Mo−C21 = 1.955(2).

their analogues of type **4**, indicating that electronic factors and steric congestion might both contribute to the comparative lability of the latter.

There is ample precedence for exclusive *anti* addition of nucleophiles to cationic diene molybdenum complexes.[8] Experimental evidence for *anti* stereoselectivity in the present series was obtained by crystallographic examination of complex **6b**. The X-ray structure provided in Figure 7 reveals the expected *anti* relationship between the metal moiety and the indolyl substituent, with the latter adopting a pseudo-axial orientation. This conformation was also apparent from two-dimensional NMR experiments (see Experimental Section).

Hydride Abstraction Experiments. The introduction of a second indole moiety into the complexes **4**, **6**, and **8** would require hydride abstraction from these allylic substrates. Hydride abstractions from allylic molybdenum complexes have most commonly been performed with trityl salts.[8] This standard method has, however, been reported to present problems when applied to more highly substituted substrates.[21] The only alternative procedures, involving the use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[21] (DDQ) or thallium(III) trifluoroacetate,[22] both under acidic conditions, seem to have been scarcely utilized. Our attempts to convert indolyl-substituted allylic substrates into cationic diene complexes have so far met with failure. When we treated **4a** with Ph_3CPF_6 in dichloromethane, cation **1** was the only molybdenum-containing product identified. This could arise from protolytic cleavage, mediated by acidic impurities derived from the trityl salt, although other pathways might be envisaged.[23] Experiments performed in the presence of hindered bases such as 2,6-di-*tert*-butylpyridine were also unsuccessful. Unfortunately, the sensitivity of the substrate toward acid excluded application of the literature procedure using DDQ and $HBF_4 \cdot Et_2O$. Although the

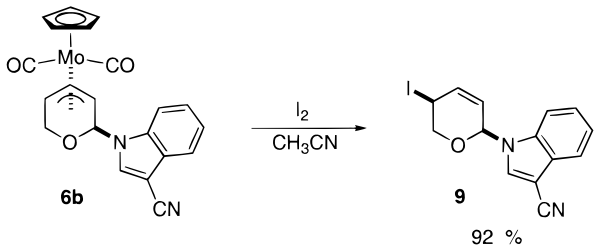

Figure 8.

complexes **6b** and **8b** also resisted hydride abstractions with trityl hexafluorophosphate, decomposition was less pronounced and substrate could in some cases be recovered after the experiment. The procedure using CH_2Cl_2/HFiP as solvent and Ph_3CBr as a precursor to the trityl cation always returned starting material.

To explore more generally the possibility of performing hydride abstractions with bulky substituents in the allylic substrate, we turned to the more stable (η^5-cyclopentadienyl)dicarbonyl[(3,4,5-η)-2-*syn*-methyl-2-*anti*-phenyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (**2b**). Treating complex **2b** with trityl cation similarly failed to convert the allylic complex into an isolable cationic diene complex. However, in a one-pot sequence incorporating solvent removal and addition of THF and MeMgBr, traces of the trisubstituted product were found. When the hydride abstraction was attempted in the NMR tube, resonances consistent with the formation of decomplexation products slowly appeared. We attribute the unsuccessful hydride abstractions to steric hindrance, since trisubstituted product was obtained, via an isolable diene complex, from the less sterically hindered **2a**. Presumably, a sluggish hydride transfer process allows competitive hydrolytic decomposition of trityl ion and protodemetalation pathways to become dominant, particularly with sensitive substrates.

Decomplexation. The synthetic utility of methods relying upon stable organometallic intermediates requires that demetalation can be performed in high yield and with good regiocontrol. Previously, decomplexation via protodemetalation with TFA has been shown with (pyranyl)molybdenum complexes.[6,7,24] Another well-known demetalation procedure relies upon treatment of an η^3 precursor with nitrosonium hexafluorophosphate and subsequent introduction of a nucleophile and exposure to oxygen.[11] Concerns related to the lability of the present indolyl-substituted substrates discouraged the application of protodemetalation. Attempts to release the organic ligand by using $NOPF_6$ followed by water[9] met with failure. Encouragingly, decomplexation was cleanly accomplished with iodine in acetonitrile at 0 °C, as exemplified for **6b** (Figure 8), which afforded the corresponding allylic iodide **9** with surprisingly high regioselectivity (NMR analysis of this material indicated the presence of only trace amounts of an isomeric iodide). NOESY experiments, together with the well-established mechanism[25] for related decomplexations, were used to corroborate the formation of the *cis*-2,5-disubstituted isomer shown in Figure 8.

(21) Green, M.; Greenfield, S.; Kersting, M. *J. Chem. Soc., Chem. Commun.* **1985**, 18. Bottrill, M.; Green, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2365.

(22) Alexander, R. P.; Stephenson, G. R. *J. Chem. Soc., Dalton Trans.* **1987**, 885.

(23) The synthetically very useful analogous behavior of a *syn*-(2-ethoxy-5,6-dihydro-2*H*-pyran-5-yl)molybdenum complex (see Figure 2) has not yet been mechanistically clarified.[6] The reversibility of the indole additions observed in this work might similarly prove useful for the resolution of cationic complexes.

(24) During the preparation of this paper, the application of additional oxidative decomplexation methods (reaction with iodine or ceric ammonium nitrate) to (pyranyl)molybdenum complexes was reported; see: Yin, J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1999**, *121*, 5811.

(25) Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; Cun-heng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748.

Conclusions. Cationic (pyran)molybdenum complexes undergo nucleophilic addition of indole derivatives in acceptable yields, stereospecifically *anti* to the metal. Oxidative cleavage of the indole adducts from the metal affords usefully functionalized indole glycoside precursors. The application of such reaction sequences to the readily available enantiomerically pure molybdenum precursors should provide a convenient entry into a variety of *N*-pyranyl- or *N*-cyclohexylindole derivatives.

Experimental Section

General Considerations. All reactions were performed under an argon atmosphere. Solvents and reagents were used as received from commercial sources, unless otherwise indicated. Dichloromethane and acetonitrile were distilled from CaH_2 under argon and stored over activated molecular sieves. Tetrahydrofuran and diethyl ether were freshly distilled from sodium/benzophenone or purchased anhydrous. Triethylamine was distilled from CaH_2. NMR spectra were recorded on a Bruker ARX400 instrument at 400.132 MHz (^{1}H) or 100.6 MHz (^{13}C). The chemical shifts are given relative to residual protio resonances of the deuterated solvent used: $CDCl_3$ δ 7.27 (^{1}H) and δ 77.2 (^{13}C); CD_2Cl_2 δ 5.32 (^{1}H) and δ 54.0 (^{13}C); CD_3CN δ 1.94 (^{1}H) and δ 118.7 (^{13}C); CD_3SOCD_3 δ 2.50 (^{1}H). IR spectra were recorded on an FT-IR Nicolet Impact 410. FAB (NBA) and EI (70 eV) mass spectra were obtained on a JEOL-SX 102 mass spectrometer. TLC analyses employed Merck aluminum-backed sheets precoated with silica gel 60 F254. Visualization was accomplished using UV light, iodine, or van Urk's reagent (1 g of *p*-(dimethylamino)benzaldehyde, 50 mL of EtOH, and 50 mL of concentrated HCl). Flash chromatography separations were performed by using Matrex silica gel. Melting points were uncorrected. Elemental analyses were obtained from H. Kolbe Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr, Germany.

(η^5-Cyclopentadienyl)dicarbonyl[6-methyl-(3,4,5,6-η)-2*H*-pyran]molybdenum Hexafluorophosphate (1). In a dry, two-necked flask flushed with argon were added dry dichloromethane (20 mL), (η^5-cyclopentadienyl)dicarbonyl-[(3,4,5-η)-2-oxo-5,6-dihydro-2*H*-pyran-5-yl]molybdenum[6] (0.77 g, 2.4 mmol), and Et_3OPF_6 (0.67 g, 2.4 mmol, 10% Et_2O). A yellow solution was obtained after a few minutes. The solution turned orange, and a new precipitate was formed after 15 min. The reaction mixture was stirred for 2 h, and the solvent was then removed. THF (20 mL) was added, and the suspension was cooled with stirring to 0 °C, whereupon a 3 M solution of MeMgBr in diethyl ether (3.0 mL, 9.0 mmol, 3.6 equiv) was added. The reaction mixture was stirred for 3 h at 0 °C and then quenched with 30 mL of saturated aqueous NH_4Cl. The mixture was warmed to room temperature and then extracted with 3 × 30 mL of dichloromethane. The combined organic phases were dried over Na_2SO_4, filtered, and evaporated, and the crude product was flash-chromatographed (degassed heptane/EtOAc, 4:1, R_f = 0.25) to give 0.70 g (80%) of (η^5-cyclopentadienyl)dicarbonyl[(3,4,5-η)-2-*syn*-ethoxy-2-methyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum as an air-sensitive yellow oil. ^{1}H NMR (CD_3CN): δ 5.32 (s, 5H), 4.39 (t, J = 7.3 Hz, 1H), 3.86 (d, J = 12.5 Hz, 1H), 3.67 (dq, J = 7.3, 1.8 Hz, 1H), 3.55 (dd, J = 7.3, 2.0 Hz, 1H), 3.53 (dd, J = 12.5, 1.8 Hz, 1H) (the two dd overlapping each other), 3.33−3.46 (m, 2H), 1.45 (s, 3H), 1.01 (t, J = 7.0 Hz, 3H). The product above (0.59 g, 1.65 mmol) was dissolved in dry dichloromethane (30 mL) and cooled to 0 °C. Ph_3CPF_6 (0.78 g, 2.0 mmol, 1.2 equiv) was added, and the reaction mixture was stirred at 0 °C for 45 min. The product was precipitated with 50 mL of diethyl ether at room temperature, and the solid was allowed to settle before the supernatant was decanted and the product triturated with 2 × 20 mL of diethyl ether. Drying under vacuum afforded 0.68 g (90%) of the title compound as a yellow solid. Mp: ∼160 °C dec. Anal. Calcd for $C_{13}H_{13}F_6MoO_3P$: C, 34.08; H, 2.86. Found: C, 33.96; H, 2.80. ^{1}H NMR (CD_3SOCD_3): δ 6.02−6.05 (m, 1H), 5.92 (s, 5H), 4.90 (br s, 1H), 4.76 (dd, J = 4.1, 1.8 Hz, 1H), 4.15 (dm, J = 14.0 Hz, 1H), 3.75 (dd, J = 14.0, 1.8 Hz, 1H), 2.32 (s, 3H); the compound was found to decompose slowly in DMSO solution. IR (KBr): 1986, 1928, 1915 cm^{-1}. HRMS (FAB+): *m/z* calcd for $C_{13}H_{13}MoO_3$ 314.9919, found M^+ 314.9922 and $(M - 2CO)^+$ 259.

(η^5-Cyclopentadienyl)dicarbonyl[(3,4,5-η)-2,2-dimethyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (2a). In a dry, two-necked flask were added the cationic complex **1** (0.37 g, 0.80 mmol) and THF (20 mL). The suspension was cooled to 0 °C, whereupon a 3 M solution of MeMgBr in diethyl ether (1.5 mL, 4.5 mmol, 5.6 equiv) was added. The reaction mixture was stirred for 2 h at 0 °C. Saturated aqueous NH_4Cl (30 mL) was added, and the reaction mixture was extracted with 3 × 20 mL of dichloromethane. The combined organic phases were dried over Na_2SO_4, filtered, and evaporated, and the crude product was flash-chromatographed (degassed CH_2Cl_2, R_f = 0.45) to give 0.23 g (88%) of a yellow solid. ^{1}H NMR (CD_3CN): δ 5.33 (s, 5H), 4.52 (t, J = 7.2 Hz, 1H), 4.03 (dm, J = 12.9 Hz, 1H), 3.71 (dd, J = 7.2, 2.0 Hz, 1H), 3.61 (dq, J = 7.2, 2.0 Hz, 1H), 3.46 (dd, J = 12.9, 2.0 Hz, 1H), 1.33 (s, 3H) and 1.16 (s, 3H). ^{13}C NMR (CD_3CN): δ 240.2, 238.4, 92.8, 71.7, 65.1, 59.9, 58.3 (br), 56.0, 31.5, 28.3. IR (NaCl plates, CH_2Cl_2): 1938, 1847 cm^{-1}. HRMS (EI, 70 eV): *m/z* calcd for $C_{14}H_{16}MoO_3$ 330.0153, found M^+ 330.0152, $(M - CO)^+$ 302, $(M - 2CO)^+$ 274.

(η^5-Cyclopentadienyl)dicarbonyl[(3,4,5-η)-2-methyl-2-phenyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (2b). In a dry, two-necked flask were added the cationic complex **1** (0.23 g, 0.50 mmol) and THF (20 mL). The suspension was cooled to 0 °C, whereupon a 1 M solution of PhMgBr in THF (2.0 mL, 2.0 mmol, 4 equiv) was added. The reaction mixture was stirred for 2.5 h at 0 °C. Saturated aqueous NH_4Cl (35 mL) was added, and the reaction mixture was extracted with 3 × 30 mL of dichloromethane. The combined organic phases were dried over Na_2SO_4, filtered, and evaporated, and the crude product was flash-chromatographed (degassed heptane/EtOAc, 4:1, R_f = 0.3) to give 0.11 g (56%) of the title product as a yellow solid. Mp: ∼140 °C dec. ^{1}H NMR (CD_3CN): δ 7.56−7.59 (m, 2H), 7.32−7.36 (m, 2H), 7.21−7.25 (m, 1H), 5.40 (s, 5H), 4.67 (t of m, J = 7.3 Hz, 1H), 4.24 (dd, J = 7.3, 2.1 Hz, 1H), 3.57−3.61 (m, 2H), 3.42 (dd, J = 13.3, 2.1 Hz, 1H), 1.36 (s, 3H). ^{13}C NMR (CD_3CN): δ 239.8, 239.3, 151.6, 128.8, 127.4, 127.2, 93.0, 75.2, 60.7, 60.3, 59.6, 59.3, 31.4. IR (KBr): 1925, 1851 cm^{-1}. HRMS (EI, 70 eV): *m/z* calcd for $C_{19}H_{18}MoO_3$ 392.0310, found M^+ 392.0314, $(M - CO)^+$ 364, $(M - 2CO)^+$ 336.

(η^5-Cyclopentadienyl)dicarbonyl[(3,4,5-η)-2,2,6-trimethyl-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (3a). The allylic complex **2a** (53 mg, 0.16 mmol) was dissolved in dry dichloromethane (13 mL) and was cooled to 0 °C. Ph_3CPF_6 (70 mg, 0.18 mmol, 1.1 equiv) was added, and the reaction mixture was stirred at 0 °C for 1 h. The product was precipitated with 40 mL of diethyl ether at room temperature, and the solid was allowed to settle before the supernatant was decanted and the product triturated with 2 × 10 mL of diethyl ether. Drying under vacuum afforded 49 mg (65%) of (η^5-cyclopentadienyl)-dicarbonyl[6,6-dimethyl-(3,4,5,6-η)-2*H*-pyran]molybdenum hexafluorophosphate as a brownish solid. ^{1}H NMR (CD_3SOCD_3): δ 8.14 (dd, J = 4.4, 2.2 Hz, 1H), 6.13−6.16 (m, 1H), 5.99 (s, 5H), 5.44 (s), traces of the allylic starting material, 5.10−5.17 (m, 2H), 1.45 (s, 3H), 1.18 (s, 3H). To the diene cation above (49 mg, 0.10 mmol) was added THF (10 mL). The suspension was cooled to 0 °C, and a 3 M solution of MeMgBr in diethyl ether (0.20 mL, 0.60 mmol, 6.0 equiv) was added. The reaction mixture was stirred at 0 °C for 4 h. Saturated aqueous NH_4Cl (30 mL) was added, and the reaction mixture was extracted with 3 × 20 mL of dichloromethane. The combined organic phases were dried over Na_2SO_4, filtered, and

evaporated, and the crude product was flash-chromatographed (CH_2Cl_2, $R_f = 0.42$) to give 13 mg (38%) of the title product as a yellow solid. ^{1}H NMR (CD_3CN): δ 5.31 (s, 5H), 4.58 (t, 7.3 Hz, 1H), 4.01 (d, $J = 7.3$ Hz, 1H), 3.95 (q, $J = 6.8$ Hz, 1H), 3.64 (d, $J = 7.3$, 1H), 1.45 (s, 3H), 1.38 (d, $J = 6.8$ Hz, 3H), 1.13 (s, 3H). ^{13}C NMR (CD_3CN): δ 240.4, 238.8, 91.9, 73.1, 69.6, 68.8, 59.4, 58.6, 38.2, 30.8, 28.6. IR (NaCl plates, CH_2Cl_2): 1940, 1859 cm^{-1}. HRMS (FAB+): *m/z* calcd for $C_{15}H_{18}MoO_3$ 344.0310, found M^+ 344.0319 and $(M - CO)^+$ 316.

General Indole Addition Procedure (Table 1). In a dry two-necked flask flushed with argon were added the indole derivative, NaH (60% dispersion in oil), and THF (10 mL) or DMF (10 mL) (**4f**). The reaction mixture was stirred for 30 min to 1 h at room temperature. The flask was cooled to 0 °C, whereupon the cationic diene complex **1**, **5**, or **7** was added. The reaction mixture was stirred for 2−3 h at 0 °C and then quenched with 20 mL of water. The mixture was warmed to room temperature and then extracted with 3 × 20 mL of dichloromethane. The isolated products were yellow solids.

(η^5-Cyclopentadienyl)dicarbonyl[(3,4,5-η)-2-*syn*-methyl-2-(3-methylindol-1-yl)-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (4a). Following the general procedure, 3-methylindole (0.19 g, 1.45 mmol, 2.2 equiv), NaH (64 mg, 1.6 mmol, 2.4 equiv), and cation **1** (0.30 g, 0.66 mmol) gave **4a**. After the combined organic phases were dried over Na_2SO_4, a few drops of triethylamine were added before passing through a silica pad. The solvent was removed under reduced pressure. Analytically pure product was obtained by trituration with ethanol (10 mL), which afforded 0.17 g (58%) of the title substance. Mp: ∼140 °C dec. Anal. Calcd. for $C_{22}H_{21}MoNO_3$: C, 59.60; H, 4.77. Found: C, 59.32; H, 4.85. ^{1}H NMR (CD_3CN): δ 7.62 (q, $J = 1.1$ Hz, 1H), 7.59 (ddd, $J = 8.0$, 1.6, 0.9 Hz, 1H), 7.49 (ddd, $J = 7.6$, 1.7, 0.8 Hz, 1H), 6.99−7.07 (m, 2H), 5.47 (s, 5H), 4.86 (t, $J = 7.1$ Hz, 1H), 4.02 (dd, $J = 7.1$, 2.2 Hz, 1H), 3.80 (dq, $J = 7.1$, 1.9 Hz, 1H), 3.42−3.43 (m, 2H), 2.32 (d, $J = 1.1$ Hz, 3H), 1.62 (s, 3H). ^{13}C NMR (CD_3CN): δ 238.5, 238.3, 173.5, 131.0, 126.9, 122.5, 120.1, 119.9, 114.9, 110.9, 94.0, 89.2, 61.2, 60.6, 60.4, 55.3, 27.2, 10.3. IR (KBr): 1934, 1861 cm^{-1}. HRMS (FAB+): *m/z* calcd for $C_{22}H_{22}MoNO_3$ 446.0654, found $(M + 1)^+$ 446.0650.

(η^5-Cyclopentadienyl)dicarbonyl[(3,4,5-η)-2-*syn*-methyl-2-(indol-1-yl)-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (4b). Following the general procedure, indole (38 mg, 0.33 mmol, 3.0 equiv), NaH (14 mg, 0.36 mmol, 3.3 equiv), and cation **1** (50 mg, 0.11 mmol) gave **4b**. The crude product was flash-chromatographed (degassed CH_2Cl_2/heptane, 2:1, with 1% of Et_3N, $R_f = 0.38$) to give 32 mg (66%) of the product. Analytically pure product was obtained by trituration with ethanol (2 mL) followed by filtration. Mp: ∼130 °C dec. ^{1}H NMR (CD_3CN): δ 7.85 (d, $J = 3.4$ Hz, 1H), 7.65 (dm, $J = 8.6$ Hz, 1H), 7.54 (dm, $J = 7.75$ Hz, 1H), 6.97−7.07 (m, 2H), 6.48 (dd, $J = 3.4$, 0.8 Hz, 1H), 5.48 (s, 5H), 4.87 (t, $J = 7.1$ Hz, 1H), 4.04 (dd, $J = 7.1$, 2.0 Hz, 1H), 3.80 (dq, $J = 7.1$, 2.0 Hz, 1H), 3.44 (dd, $J_{AB} = 12.5$ Hz, $J = 1.9$ Hz, 1H), 3.37 (d, $J_{AB} = 12.5$ Hz, 1H), 1.66 (s, 3H). ^{13}C NMR (CD_3CN): δ 240.4, 239.2, 137.1, 130.9, 129.2, 122.5, 121.9, 120.8, 115.1, 102.1, 94.0, 89.6, 61.2, 60.7, 60.5, 55.1, 27.3. IR (NaCl plates, CH_2Cl_2): 1938, 1861 cm^{-1}. HRMS (FAB+): *m/z* calcd for $C_{19}H_{19}MoNO$ 375.0521, found $(M - 2CO)^+$ 375.0532.

(η^5-Cyclopentadienyl)dicarbonyl[(3,4,5-η)-2-*syn*-methyl-2-(2-oxoindolin-3-yl)-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (4f). Following the general procedure, 2-indolinone (0.23 g, 1.70 mmol, 5.5 equiv), NaH (65 mg, 1.6 mmol, 5.2 equiv), and cation **1** (0.14 g, 0.31 mmol) gave **4f**. The combined organic phases were further extracted with 3 × 100 mL of water, dried over Na_2SO_4, filtered, and evaporated. The crude product was flash-chromatographed (degassed CH_2Cl_2/MeOH/Et_3N, 95:4:1, $R_f = 0.45$) to give 55 mg (40%) of **4f**. ^{1}H NMR (CD_3CN): δ 8.37 (br s, 1H), 7.13−7.22 (m, 2H), 6.93 (dt, $J = 7.7$, 1.0 Hz, 1H), 7.49 (dm, $J = 7.7$ Hz, 1H), 5.40 (s, 5H), 4.66 (t, $J = 7.3$ Hz, 1H), 4.53 (dd, $J = 7.3$, 2.2 Hz, 1H), 4.26 (dm, $J = 13$ Hz, 1H), 3.76−3.80 (m, 2H), 3.70 (dd, $J = 13$, 1.7 Hz, 1H), 0.81 (d, $J = 0.8$ Hz, 3H). ^{13}C NMR (CD_3CN): δ 240.1, 239.0, 178.3, 143.4, 129.2, 128.9, 127.9, 122.9, 110.1, 93.5, 76.5, 64.2, 61.1, 59.4, 58.7, 57.3, 21.9. IR (NaCl plates, CH_2Cl_2): 1942, 1863, 1703 cm^{-1}. HRMS (FAB+): *m/z* calcd for $C_{21}H_{19}MoNO_4$ 447.0368, found M^+ 447.0383, $(M - CO)^+$ 419, $(M - 2CO)^+$ 391.

(η^5-Cyclopentadienyl)dicarbonyl[(3,4,5-η)-2-*syn*-methyl-2-(3-(hydroxymethyl)indol-1-yl)-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (4h). Following the general procedure, 3-(hydroxymethyl)indole (20 mg, 0.14 mmol, 1.3 equiv), NaH (6.7 mg, 0.16 mmol, 1.5 equiv), and cation **1** (49 mg, 0.11 mmol) gave **4h**. The combined organic phases were dried over Na_2SO_4, filtered, and evaporated. The crude product was flash-chromatographed (degassed CH_2Cl_2/MeOH/Et_3N, 95:4:1, $R_f = 0.52$) to give 20 mg (41%) of **4h**. ^{1}H NMR (CD_3CN): δ 7.82 (s, 1H), 7.60−7.64 (m, 2H), 7.02−7.09 (m, 2H), 5.47 (s, 5H), 4.86 (t, $J = 7.0$ Hz, 1H), 4.77 (s, 2H), 4.02 (dd, $J = 7.0$, 2.2 Hz, 1H), 3.79 (dq, $J = 7.0$, 1.9 Hz, 1H), 3.44 (dd, $J_{AB} = 12.9$ Hz, $J = 1.8$ Hz, 1H), 3.40 (dm, $J_{AB} = 12.9$ Hz, 1H), 1.65 (s, 3H). IR (NaCl plates, CH_2Cl_2) :1944, 1865 cm^{-1}. Due to the instability of the product and difficulties in the purification no further analyses were performed.

(η^5-Cyclopentadienyl)dicarbonyl[(3,4,5-η)-2-*anti*-(3-methylindol-1-yl)-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (6a). Following the general procedure, 3-methylindole (69 mg, 0.52 mmol, 1.2 equiv), NaH (22 mg, 0.55 mmol, 2.2 equiv), and cation **5** (97 mg, 0.25 mmol) gave **6a**. The combined organic phases were dried over Na_2SO_4, filtered, and evaporated. The crude product was flash-chromatographed (degassed CH_2Cl_2/heptane, 1:1, with 1% Et_3N, $R_f = 0.3$) to give 28 mg (52%). The product was triturated with ethanol to give analytically pure material. Mp: ∼150 °C dec. ^{1}H NMR (CD_3CN): δ 7.80 (d, $J = 1.1$ Hz, 1H), 7.53 (ddd, $J = 8.1$, 1.4, 1.2 Hz, 1H), 7.31 (d, $J = 8.1$ Hz, 1H), 7.05−7.15 (m, 2H), 5.80 (d, $J = 2.1$ Hz, 1H), 5.51 (s, 5H), 4.98 (t, $J = 7.1$ Hz, 1H), 3.77 (dq, $J = 7.1$, 1.8 Hz, 1H), 3.58 (dt, $J = 7.1$, 2.1 Hz, 1H), 3.52 (d, $J_{AB} = 12.4$ Hz, 1H), 3.28 (dd, $J_{AB} = 12.4$ Hz, $J = 2.2$ Hz, 1H), 2.34 (d, $J = 1.1$ Hz, 3H). ^{13}C NMR (CD_3CN): δ 237.7, 236.4, 138.3, 131.1, 124.7, 122.9, 120.7, 120.0, 111.7, 111.5, 94.2, 78.7, 58.1, 57.5, 55.0, 48.9, 10.2. IR (KBr): 1938, 1867 cm^{-1}. HRMS (FAB+): *m/z* calcd for $C_{21}H_{20}MoNO_3$ 432.0497, found $(M + 1)^+$ 432.0490 and $(M - 2CO)^+$ 375.

(η^5-Cyclopentadienyl)dicarbonyl[(3,4,5-η)-2-*anti*-(3-cyanoindol-1-yl)-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (6b). Following the general procedure, 3-cyanoindole (167 mg, 1.18 mmol, 3.0 equiv), NaH (48 mg, 1.2 mmol, 3.1 equiv), and cation **5** (150 mg, 0.39 mmol) gave **6b**. The combined organic phases were dried over Na_2SO_4, filtered, and evaporated. The crude product was flash-chromatographed (degassed CH_2Cl_2/heptane, 2:1, with 1% Et_3N, $R_f = 0.16$) to give 120 mg (70%) of a yellow solid. Mp: ∼140 °C dec. ^{1}H NMR[26] (CD_3CN): δ 8.67 (s, 1H), 7.69−7.72 (m, 1H), 7.49−7.52 (m, 1H), 7.27−7.34 (m, 2H), 5.88 (d, $J = 1.9$ Hz, 1H, 2-H), 5.53 (s, 5H), 4.99 (t, $J = 7.1$ Hz, 1H, 4-H), 3.78 (dq, $J = 7.1$, 2.0 Hz, 1H, 5-H), 3.59 (dt, $J = 7.1$, 1.9 Hz, 1H, 3-H), 3.45 (d, $J_{AB} = 12.6$ Hz, 1H, *anti*-6-H), 3.32 (dd, $J_{AB} = 12.6$ Hz, $J = 2.0$ Hz, 1H, *syn*-6-H). ^{13}C NMR (CD_2Cl_2): δ 235.4, 233.9, 136.6, 133.6, 128.8, 124.4, 123.1, 120.0, 116.4, 112.5, 93.3, 86.5, 79.6, 57.4, 55.7, 54.0 (obscured by the solvent signal), 45.8. IR (KBr): 2218, 1946, 1865 cm^{-1}. HRMS (FAB+): *m/z* calcd for $C_{19}H_{16}ON_2Mo$ 386.0317, found $(M - 2CO)^+$ 386.0352.

(η^5-Cyclopentadienyl)dicarbonyl[(3,4,5-η)-2-*anti*-(3-formylindol-1-yl)-5,6-dihydro-2*H*-pyran-5-yl]molybdenum (6c). Following the general procedure, 3-formylindole (95

(26) Proton assignments were based on NOESY experiments, which revealed correlations e.g. between the cyanoindolyl 2′-H and 3-H, 4-H, and *anti*-6-H as well as between 2-H and 3-H. The NOESY spectrum obtained was fully consistent with the conformation, having a pseudo-axial cyanoindolyl substituent, observed crystallographically.

mg, 0.65 mmol, 5.0 equiv), NaH (25 mg, 0.64 mmol, 4.9 equiv), and cation **5** (50 mg, 0.13 mmol) gave **6c**. The combined organic phases were dried over Na_2SO_4, filtered, and evaporated. The crude product was flash-chromatographed twice (degassed CH_2Cl_2/MeOH/Et_3N, 98:1:1, $R_f = 0.3$) to give 27 mg (47%) of the title compound. Mp: ~140 °C dec. ^{1}H NMR (CD_3CN): δ 10.10 (s, 1H), 8.58 (s, 1H), 8.21−8.24 (m, 1H), 7.46−7.50 (m, 1H), 7.27−7.31 (m, 2H), 5.89 (d, $J = 2.0$ Hz, 1H), 5.50 (s, 5H), 4.90 (t, $J = 7.0$ Hz, 1H), 3.76 (dq, $J = 7.0$, 2.0 Hz, 1H), 3.55 (dt, $J = 7.0$, 2.0 Hz, 1H), 3.56 (d, $J_{AB} = 12.6$ Hz, 1H), 3.40 (dd, $J_{AB} = 12.6$ Hz, $J = 2.0$ Hz, 1H). ^{13}C NMR (CD_2Cl_2): δ 235.3, 233.8, 185.2, 138.3, 136.7, 126.2, 124.4, 123.6, 121.9, 118.5, 111.9, 93.2, 79.4, 57.2, 55.6, 54.0 (obscured by the solvent signal), 45.7. IR (KBr): 1946, 1876, 1651 cm^{-1}. HRMS (FAB+): *m/z* calcd for $C_{19}H_{16}MoN_2O$ 389.0313, found $(M - 2CO)^+$ 389.0321.

(η^5-Cyclopentadienyl)dicarbonyl[(1,2,3,4-η)-cyclohexadiene]molybdenum Hexafluorophosphate (7). In a Schlenk flask were placed degassed 1,1,1,3,3,3-hexafluoro-2-propanol (2.5 mL), dichloromethane (7.5 mL), and (η^5-cyclopentadienyl)dicarbonyl[(1,2,3-η)-1-cyclohexen-3-yl]molybdenum (0.30 g, 1.0 mmol).[11] The flask was sequentially flushed with argon and evacuated several times. The flask was cooled to 0 °C, whereupon bromotriphenylmethane (370 mg, 1.1 mmol, 1.1 equiv) dissolved in degassed dichloromethane (2 mL) was added, and the reaction mixture was stirred at 0 °C for 1 h. Degassed diethyl ether (40 mL) was added, and the solid was allowed to settle before the supernatant was removed. The product was then washed with 2 × 10 mL of diethyl ether, leaving, after drying under vacuum, 0.32 g (85%) of (η^5-cyclopentadienyl)dicarbonyl[(1,2,3,4-η)-cyclohexadiene]molybdenum bromide. Mp: ~140 °C dec. Anal. Calcd for $C_{13}H_{13}BrMoO_2$: C, 41.41; H, 3.48. Found: C, 41.22; H, 3.62. ^{1}H NMR (CD_2Cl_2): δ 6.50 (br s, 2H), 6.00 (s, 5H), 5.00 (br s, 2H), 2.25 (br d, $J = 13.0$ Hz, 2H), 2.02 (br d, $J = 13.0$ Hz, 2H). ^{13}C NMR (CD_2Cl_2): δ 225.1, 94.9, 89.4, 84.8, 24.6. IR (KBr): 2000, 1934 cm^{-1}. HRMS (FAB+): *m/z* calcd for $C_{13}H_{13}MoO_2$ 298.9969, found M^+ 298.9963. The bromide was dissolved in 50 mL of water, and ammonium hexafluorophosphate (1.5 g, 9.2 mmol) was added. The counterion exchange occurred immediately, and a yellow precipitate was formed. The product was collected by filtration, leaving 0.30 g (80%) of **7**.[11]

(η^5-Cyclopentadienyl)dicarbonyl[(2,3,4-η)-1-*anti*-(3-methylindol-1-yl)-2-cyclohexen-4-yl]molybdenum (8a). Following the general procedure, 3-methylindole (0.13 g, 1.0 mmol, 3.0 equiv), NaH (41 mg, 1.0 mmol, 3.0 equiv), and cation **7** (0.15 g, 0.34 mmol) gave **8a**. After the combined organic phases were dried over Na_2SO_4, triethylamine (1 mL) was added before passing through a silica pad. The solvent was removed under reduced pressure. The crude product was flash-chromatographed (degassed CH_2Cl_2/heptane, 2:1, with 1% Et_3N, $R_f = 0.4$) to give 62 mg (42%) of **8a**. Mp: ~120 °C dec. Anal. Calcd for $C_{22}H_{21}MoNO_2$: C, 61.83; H, 4.95. Found: C, 61.43; H, 4.90. ^{1}H NMR (CD_3CN): δ 7.50−7.53 (m, 2H), 7.30 (d, $J = 8.5$ Hz, 1H), 7.13 (ddd, $J = 8.5$, 7.0, 1.0 Hz, 1H), 7.03 (ddd, $J = 7.9$, 7.0, 1.0 Hz, 1H), 5.44 (s, 5H), 4.65−4.69 (m, 1H), 4.67 (t, $J = 7.0$ Hz, 1H), 3.99−4.03 (m, 1H), 3.56−3.60 (m, 1H), 2.34 (d, $J = 1.0$ Hz, 3H), 2.08−2.23 (m, 1H) obscured by the water signal, 1.69−1.78 (m, 1H), 0.94−1.14 (m, 2H). ^{13}C NMR (CD_3CN): δ 238.6, 237.0, 137.4, 130.3, 124.3, 122.5, 120.11, 119.9, 111.4, 110.5, 94.2, 60.2, 58.0, 51.9, 51.1, 25.9, 20.3, 10.2. IR (KBr): 1940, 1849 cm^{-1}. HRMS (FAB+): calcd for $C_{22}H_{21}MoNO_2$ 429.0626, found M^+ 429.0630.

(η^5-Cyclopentadienyl)dicarbonyl[(2,3,4-η)-1-*anti*-(3-cyanoindol-1-yl)-2-cyclohexen-4-yl]molybdenum (8b). Following the general procedure, 3-cyanoindole (40 mg, 0.28 mmol, 2.5 equiv), NaH (11 mg, 0.28 mmol, 2.5 equiv), and cation **7** (50 mg, 0.11 mmol) gave **8b**. The combined organic phases were dried over Na_2SO_4, filtered, and evaporated. The crude product was flash-chromatographed (degassed CH_2Cl_2/heptane, 2:1, with 1% Et_3N, $R_f = 0.2$) to give 30 mg (61%) of the title product. ^{1}H NMR (CD_2Cl_2): δ 8.31 (s,1H), 7.73 (dq, $J = 7.2$, 1.7, 1.4 Hz, 1H), 7.46 (dm, $J = 8.0$ Hz, 1H), 7.25−7.34 (m, 2H), 5.42 (s, 5H), 4.77−4.81 (m, 1H), 4.62 (t, $J = 6.8$ Hz, 1H), 4.00−4.05 (m, 1H), 3.52−3.57 (m, 1H), 2.01−2.11 (m, 1H), 1.74−1.82 (m, 1H), 1.04−1.24 (m, 2H). ^{13}C NMR (CD_2Cl_2): δ 236.6, 234.6, 135.8, 133.6, 128.7, 124.0, 122.6, 120.1, 116.7, 111.3, 93.3, 85.7, 58.8, 57.5, 52.5, 48.9, 25.1, 18.9. IR (KBr): 2214, 1940, 1859, 1844 cm^{-1}. HRMS (FAB+): *m/z* calcd for $C_{22}H_{18}O_2N_2Mo$ 440.0422, found M^+ 440.0405 and $(M - CO)^+$ 412.

Table 2. Crystallographic Data for Complex 6b

formula	$C_{21}H_{16}MoN_2O_3$
fw	440.30
cryst size, mm^3	0.19 × 0.13 × 0.10
cryst syst	monoclinic
space group	*C*2/*c* (No. 15)
a, Å	21.575(4)
b, Å	14.910(3)
c, Å	12.837(3)
α, deg	90.00
β, deg	118.09(3)
γ, deg	90.00
V, Å^3	3642.9(13)
Z	8
d_{calcd}, g cm^{-3}	1.606
diffractometer	smart CCD system
temp, K	293(2)
μ, mm^{-1}	0.744
scan method	ω
2θ(max), deg	64.38
abs cor	empirical
T_{min}	0.872
T_{max}	0.929
h	−28 to +32
k	−22 to +22
l	−18 to +12
total no. of rflns	17 867
no. of unique rflns	5824
no. of obsd rflns ($>2\sigma(I)$)	4284
no. of params refined	244
R	0.0303
R_w	0.0730
min/max resid electron density, e Å^{-3}	−0.575/0.451

Oxidative Decomplexation. Complex **6b** (57 mg, 0.13 mmol) was dissolved in acetonitrile (5 mL), and the flask was cooled to 0 °C before iodine (0.10 g, 0.40 mmol, 3.1 equiv) was added. The reaction mixture was stirred at 0 °C for 30 min. Water (25 mL) was added, and the reaction mixture was extracted with 2 × 20 mL of dichloromethane. The combined organic phases were washed with 2 × 20 mL of aqueous sodium thiosulfate solution and then with 2 × 10 mL of water, dried over Na_2SO_4, filtered, and evaporated to give 56 mg of crude material. The crude product (18 mg) was flash-chromatographed (CH_2Cl_2, $R_f = 0.66$) to give 17 mg (92%) of iodide **9**. The ^{1}H NMR spectrum obtained for this material showed minor peaks (δ 6.51, 5.93, 3.75) indicative of the presence of a small amount (approximately 5%) of an isomer. Strong NOESY correlations primarily between the signals at δ 4.04, 4.85−4.90, and 6.35 were used to assign the structure of the major component **9**. ^{1}H NMR ($CDCl_3$): δ 7.79 (s, 1H), 7.79 (ddd, $J =$ 7.7, 1.3, 1.5 Hz), 7.63 (dm, $J = 8.1$ Hz), 7.33−7.42 (m, 2H), 6.68 (dddd, $J = 10.1$, 3.3, 2.0, 0.5 Hz, 1H), 6.35 (q, $J = 2.0$ Hz, 1H), 5.87 (ddd, $J = 10.1$, 2.8, 2.0 Hz, 1H), 4.85−4.90 (m, 1H), 4.04 (ddd, $J_{AB} = 12.5$ Hz, $J = 4.9$, 0.5 Hz, 1H), 3.94 (dd, $J_{AB} =$ 12.5 Hz, $J = 7.2$ Hz, 1H). ^{13}C NMR (CD_3Cl_3): δ 136.4, 135.5, 133.7, 128.3, 124.7, 123.9, 123.2, 120.2, 115.6, 111.5, 87.9, 77.9, 68.0, 17.0. IR (NaCl plates, CH_2Cl_2): 3122, 3053, 2922, 2848, 2220, 1531, 1460, 1232, 1176 cm^{-1}. HRMS (FAB+): *m/z* calcd for $C_{14}H_{12}IN_2O$ 350.9994, found $(M + 1)^+$ 350.9991.

X-ray Structure Analysis of Compound 6b. Single crystals were grown from deuterated chloroform. The crystal

data and details of the data collection and refinement are given in Table 2. Figure 7 shows a DIAMOND[27] drawing. Intensity data were collected at 293 K with a SMART CCD system using ω scan and a rotating anode with Mo Kα radiation (0.710 73 Å).[28] No decay was observed during the data collection. All reflections were merged and integrated using SAINT.[29] All reflections were corrected for Lorentz and polarization effects as well as absorption.[30]

The structure was solved by direct methods using SHELXS97,[31] while the structure refinement was performed on F^2 using SHELXL97.[32] All non-hydrogen atoms were refined with anisotropic displacement parameters, while the hydrogen atoms were constrained to the parent site, using a riding model. No high electron density residues were found in the structure.

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Supporting Information Available: Representative ^{1}H and ^{13}C NMR spectra for compounds **1**, **2a**,**b**, **3a**, **4a**,**b**,**f**, **6a**−**c**, **7**, **8a**,**b**, and **9** and complete crystallographic data, including bond distances and angles, for complex **6b.** This material is available free of charge via the Internet at http://pubs.acs.org.

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